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CYANOACETYLENE. PART I. SYNTHESIS AND SOME CHEMICAL PROPERTIES.

Sunsuke Murahashi, Takeo Takizawa, Shohei Kurioke, and Shoji Maekawa

Introduction

The historic studies on cyanoacetylene in addition to the researches of Moureu[1] includes only the work of Westernberg[2] who synthesized a small amount of this material following the Moureu method and used this material to make microwave measurements of the C≡C and C≡N bonds. These were the only reports on this subject. Acrylonitrile which is a compound with molecule of hydrogen added to cyanoethylene is manufactured on a very large industrial scale from acetylene and hydrocyanic acid, and its chemistry is described in volumes of chemical literature[3]. In contrast, the literature on cyanoacetylene is surprisingly sparse[4]. In view of the lack of material on this subject, we set out to accumulate as much information as we could as well as to seek an industrial method of preparation and associated fields of application. Part 1 describes an improvement of the Moureu synthesis (Takeo Takizawa, Shohei Kurioka) along with some of the properties of cyanoacetylene (Takeo Takizawa, Shoji Maekawa).

The Moureu synthesis goes stepwise from the conversion of acetylene to propiolic acid, then the amide, and dehydration to yield the nitrile according to steps I-V shown below.

$$HC{\equiv}CH + Na \xrightarrow[\text{(I)}]{\text{Liq. } NH_3} HC{\equiv}C\text{-}Na$$

$$\xrightarrow[\text{(I)}]{CO_2} HC{\equiv}C\text{-}COONa$$

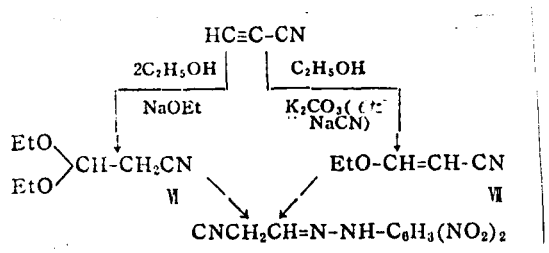
$$\xrightarrow{H_2SO_4} HC{\equiv}C\text{-}COOH \xrightarrow[\text{(II)}]{C_2H_5OH} HC{\equiv}C\text{-}CO_2C_2H_5$$

$$\xrightarrow[\text{(IV)}]{NH_3} HC{\equiv}C\text{-}CONH_2 \xrightarrow[\text{(V)}]{-H_2O} HC{\equiv}C\text{-}CN$$

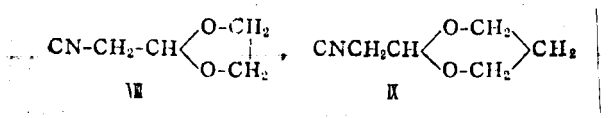
* Numbers in the margin indicate pagination in the original foreign text.

The yields in the steps for amide formation and its dehydration were poor in the originally devised synthesis which made the overall yield poor. We substituted in step IV the amide formation in liquid ammonia at low temperature and succeeded in obtaining good yield (95%). In the dehydration of step V, P_2O_5 was suspended in dry xylol to which medium the amide was placed. This improved the yield to 81% for this step, and these two steps gave a much greater overall yield than obtainable by the original Moureu process. When the propiolic acid ester was being converted to the amide by a procedure other than that mentioned above, yellow powdery material believed to be a polymer was formed which greatly reduced the overall yield.

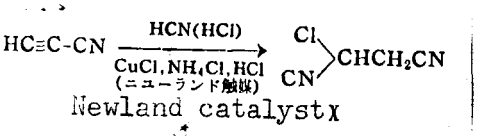
The cyanoethylene so obtained had a mp of 5°C and bp of 42.5°C which agreed with the values of Moureu. Its vapor is extremely lachrymatory, it is easily combustible, and it burns the skin on contact. The burn does not respond readily to treatment. It dissolves readily in the oridinary organic solvents and dissolves in 200 times its volume of water. When stored in an ampoule, it gradually acquires a violet color. When this is distilled, a very small residue that is very highly colored remains while colorless cyanoethylene is recovered in the distillate. This material is stable in dilute mineral acids undergoing no change even after long contact time. On the other hand, it is unstable in alkaline medium and turns dark purple immediately to end up as a dark and gluey material. Placing this compound in ammoniacal copper or silver solution results in the formation of a yellow-green or white precipitate which will explode when placed near a flame in the dry condition. This is a property that is common to many of the metallic acetylides. It readily adds on alcohol. It picks up two molecules of alcohol in the presence of sodium alcoholate to form diethyl acetal. In the presence of potassium carbonate (or sodium cyanide) catalyst, it adds a molecule of alcohol to form a vinyl ether (see the next reaction). This product is hydrolyzed by mineral acid and the product forms yellow crystals with dinitrophenylhydrazine which is dinitrophenylhydrazone of cyanoacetoaldehyde.



Reaction with ethylene glycol or trimethylene glycol gives the respective ring acetal.



The addition of hydrocyanic acid to cyanoacetylene takes place in the presence of Cu(I) catalyst. There is a simultaneous addition of HCl, and the product is α-chlorosuccinnonitrile (next reaction).



The same product is formed even when HCl is not added. The following secondary reaction is thought to account for this behavior.

$$CuCl + HCN \rightleftarrows CuCn + HCl$$

When cyanoacetylene together with benzoyl peroxide catalyst is heated 10 hours in a sealed tube at 70°C, it undergoes no change, and the bulk of the material is recovered unchanged on distillation. Thus, it seems that it has no tendency to undergo radical polymerization. On the other hand, it immediately turns dark at room temperature on the addition of aluminum chloride and solidifies. This indicates a ready tendency toward ionic polymerization.

Experimental

Propiolic Acid

Metallic sodium and acetylene were introduced simultaneously into liquid ammonia[5] to form the sodium acetylide. The ammonia was nearly completely driven off after which the residue was suspended in dry xylol. The suspension was placed in an autoclave and pressurized with CO_2 gas (initial pressure 50-60 atm) while being stirred at room temperature. Absorbed CO_2 was replenished, and the reaction pressure was maintained at 40-60 atm. This carboxylation required a long time. Results of this synthesis are shown in Table 1.

Table 1

実験番号 (1)	液体アンモニア (2) (cc)	Na (g)	反応時間 (3) (day)	CO_2の吸収量 (見掛け) (4) (l)	(%)	HC≡C-COOH (g)	(%)	HO_2C-C≡C-CO_2H (粗) (g) (5)	Na よりのカルボン酸収率 (%) (6)
1	500	23	2	11	(50)	—	26.7	—	
2	600	21.5	9	6.6	(31.5)	27.2	41.5	11.0	44.9
3	700	36.0	7	20.3	(57.8)	58.3	53.5	11.0	65.6
4	1400	64	10	14	(23.2)	83.2	44.3	26.0	60.8
5	1400	72	5	26.0	(37.1)	119.5	54.7	42.0	78.3
6	500	32.5	5	—	—	38.2	38.7	15.0	50.5
7	1400	85	16	32.8	(40)	164.0	63.5	23.5	74.5

Key: 1. run no.
2. liquid ammonia (cc)
3. reaction time (day)
4. CO_2 absorbed (apparent)
5. (crude)
6. carboxylic acid yield from Na (%)

Table 2

No. (1)	アミド (g)	P_2O_5 (g)	溶媒 (2) (g)	シアノアセチレン (3) (g)	(%)
1	3	10	なし (4)	1.1	49.6
2	5	17	なし (4)	1.0	27.1
3	5	20	トルオール 30	2.2	59.6
4	15	25	〃 (5) 25	7.7	69.5
5	20	42	〃 45	10.4	70.5
6	5	15	キシロール (6) 35	3.0	81.5

Key: 1. amide (g)
2. solvent (g)
3. Cyanoacetylene
4. none
5. toluol
6. xylol

The following reaction seems applicable to form acetylene dicarboxylic acid.

$$HC{\equiv}C\text{-}Na \longrightarrow HC{\equiv}C\text{-}COONa$$

$$HC{\equiv}C\text{-}COONa + HC{\equiv}C\text{-}Na \rightleftharpoons NaC{\equiv}C\text{-}COONa + HC{\equiv}CH$$

$$NaC{\equiv}C\text{-}COONa + CO_2 \longrightarrow NaOOC\text{-}C{\equiv}C\text{-}COONa$$

Consequently, carrying out carboxylation in the presence of pressurized acetylene should control the formation of acetylene dicarboxylic acid. Actually, run No. 7 was carried out under an acetylene pressure of 20 atm, and some limitation to the formation of the dicarboxylic product was seen. The sodium acetylide produced from 760 g of metallic sodium was suspended in 10 ℓ of xylol. This large scale experiment was run only once, and the results were not very favorable. The yield was 800 g propiolic acid, 150 g acetylene dicarboxylic ester (35.3% and 5.3% yields respectively), and 30 g of highly noxious liquid.

Propiolic Acid Ester

Catalyst of toluenesulfonic acid and benzene-alcohol-water azeotrope were utilized for the dehydration step to produce the ester. The product had bp_{175} 75-76°C (87-75% yield).

Other products included one with bp_{21} 92-93°C which agreed with that of β , β -dimethoxy propionic acid ester and another with bp_{2-3} 170-180°C which seemed to be the trimesic acid ester. In other words, a product that corresponded to a trimer ring polymer of propiolic acid was formed.

Propiolic Amide

The amide reaction of propiolic acid in liquid ammonia gives the maximum yield of amide. It was found that the presence of water in the ammonia, the presence of alcohol in the ammonia, too short reaction time, and increased reaction time all contributed to low yield of amide. Suitable conditions include placing 100 g of propiolic ester drop by drop in 500 cc of liquid ammonia (-60°C), holding this temperature for 16-20 hours, warming to room temperature to let the ammonia evaporate away, and drying under vacuum. Light yellow crystals of the amide are then obtained in good yield. In the aggregate of five runs, 335 g of amide was obtained from 500 g of ester. This is a yield of 95%. This product can be used as is for the next reaction. Its mp was 61-62°C agreeing with the Moureu value.

Cyanoacetylene

This reaction involved heating, and the atmosphere within the reaction vessel was displaced with nitrogen. Dehydration was by boiling in xylol in which free P_2O_5 was suspended. The product cyanoethylene was cooled to 6-8°C, collected, and purified by redistillation.

β , β -Dimethoxy Propiolic Nitrile

Metallic sodium (0.4 g) was dissolved in 20 cc methanol, and cooled 4 g cyanoethylene was added (in 20 cc methanol) drop by drop with stirring. The reaction was vigorous, and the contents heated up to 10°C even though the vessel was being cooled. The alkali was neutralized once the reaction was over, the solution was concentrated, and it was extracted with ether.

This extract was washed with water, dried, and distilled. The product had bp_{30} 92.5°C, yield 4.6 g (50.8%) n_D^{20} 1.4130.

Analysis	C 51.78%,	H 7.37%	N 12.13%
Calculated as $C_5H_9NO_2$	C 52.17%,	H 7.82%	N 12.17%

β ,β'-Diethoxy Propionitrile (VI)

The same procedure as above was carried out in ethanol, and a 78% yield was obtained. bp_{10} 82°C, n_D^{21} 1.4140.

Analysis	C 57.74%*	H 9.38%,	N 9.59%
Calculated as $C_7H_{13}NO_2$	C 58.7%,	H 9.09%,	N 9.78%

When both compounds are treated with 2,4-dinitrophenyl hydrazine-sulfuric acid solution, they hydrolyze to form the 2,4-dinitrophenyl hydrazone of cyanoacetoaldehyde which are yellow crystals with mp 168.5-169.5°C**.

Analysis	C 43.68%,	H 2.98%,	N 28.15%
Calculated as $C_9H_7N_5O_4$	C 43.37%,	H 2.81%,	N 28.11%

When the alcohol addition is carried out with a weak base like sodium cyanide, the difficulty dissociable compounds like VI and VII are formed. Analysis by the lauryl mercaptan method[7] showed about 30% content of VII. The reaction was carried out with 0.04 g sodium cyanide, 2 g cyanoacetylene, and 10 cc ethanol at 0°C. Product of bp_{20} 97°C and 3.2 g yield was obtained.

2-Cyanomethyldioxolan (XIII)

This product was obtained by reacting 1 g cyanoacetylene, 5 g ethylene glycol, 1 g metallic sodium (dissolved in 5 g ethylene glycol) in the manner described above. The yield was 1.2 g of colorless viscous liquid with bp_{13} 95°C, n_D^{20} 1.4354.

Analysis	N 12.38%
Calculated as $C_5H_7NO_2$	

* S. M. McElvain (J. Am. Chem. Soc. 69, 2657 (1957) reported the separation of β ,β -diethoxy propionitrile and β -ethoxyacrylonitrile to be difficult. The discrepancy in the analytical values is attributed to the presence of small amount of vinyl impurity.

** The crude crystals have mp 190-194°C. Repeated recrystallizations from ethyl acetate lowered the mp to 169.5°C which was the lower limit.

2-Cyanomethyl-1,3-Dioxane (IX)

In the same manner as before, 2 g cyanoacetylene was reacted with trimethylene glycol in cold tetrahydrofuran solvent, and 2.0 g of oily product of bp_4 93°C was obtained. n_D^{20} 1.4460

Analysis	C 57.03%,	H 7.64%,	N 11.64%
Calculated as $C_6H_9NO_2$	C 56.68%,	H 7.14%,	N 11.02%

Chlorosuccinnonitrile (X)

Cyanoacetylene was reacted with hydrogen cyanide in the presence of Newland catalyst at 30°C in a sealed tube. The white precipitate which formed initially eventually redissolved, and an oily liquid separated. The oily product was collected and distilled. bp_{80} 74°C, noxious, mobile liquid.

Analysis	C 41.02%,	H 2.66%
Calculated as $C_4H_4ClN_2$	C 41.92%,	H 2.62°

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[6] C. K. Ingold, J. Chem. Soc. 127, 1199 (1925).

[7] D. W. Beesing et al., Anal. Chem. 21, 1073 (1949).